

# **Design and Scalable Assembly of High Density Low Tortuosity Electrodes**

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Presenter:

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Project ID: ES071

# Overview

## Timeline

- Project start: May 22, 2013
- Project end: April 3, 2017
- 25% complete

## Budget

- Total project funding
  - DOE share: \$1,075,344
  - Contractor share: \$0
- Funding received in FY13
  - \$256,983
- Funding for FY14
  - \$265,637

## Barriers

- Lowering cost and increasing energy density of Li-ion batteries by reducing inactive content
- Achieve 3x times the area capacity (mAh/cm<sup>2</sup>) of current technology under EV duty cycles
- Achieving sufficient electronic conductivity in additive-free dense thick electrodes.

## Partners

**Collaborations:** Antoni P. Tomsia, LBNL

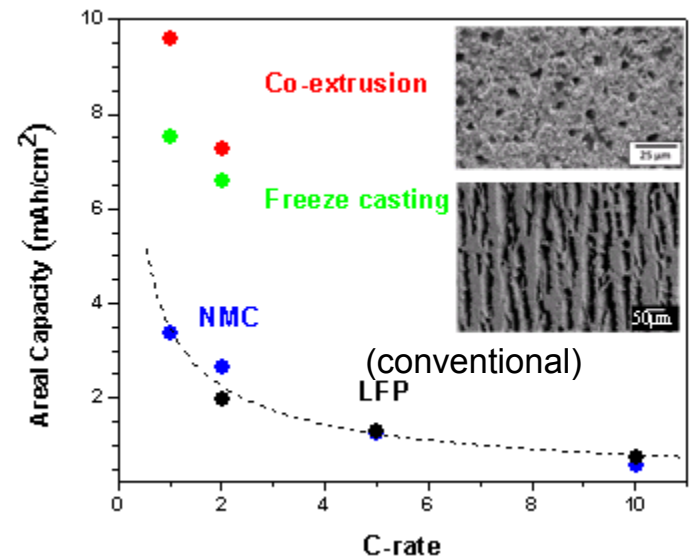
- Sample fabrication

Project lead: MIT

# Relevance

- The high inactive materials content of current Li-ion batteries contributes directly to high battery cost, and reduces specific energy and energy density.
- The number of separator and current collector layers per Ah of cell capacity is inversely proportional to the area capacity (mAh/cm<sup>2</sup>) of the electrode.
- Area capacity can be increased arbitrarily by increasing electrode thickness and/or density, but does not contribute *usable* energy unless the capacity can be accessed at practical C-rates.
- Thus, concepts that can provide higher usable area capacity, e.g. during ~2C pulses in a EV or PHEV drive cycle, are needed.
- Binder-free, thick electrodes with low tortuosity porosity is one such approach, previously demonstrated in LiCoO<sub>2</sub> cathodes:

(Bae et al. *Adv.Mater.* 2013, 25, 1254–1258, and present work.)



# Objectives

**Overall Objective:** Develop a scalable high density binder-free low-tortuosity electrode design and fabrication process to enable increased cell-level energy density compared to conventional Li-ion technology.

## Objectives in detail (March 2013 – March 2014):

- Measure electronic and ionic transport in candidate cathode materials as a function of lithium content and temperature, using additive-free sintered dense samples to obtain results for the pure material.
- In addition to  $\text{LiCoO}_2$  (previously validated) and NMC (previously ruled out for low electronic conductivity), candidates are  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (**NCA**),  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_{4-\delta}$  (**LMNO**) and  $\text{LiMn}_{1.5}\text{Ni}_{0.5-y}\text{Fe}_y\text{O}_{4-\delta}$  (**Fe-LMNO**).
- Down-select cathodes for further work based on electronic and ionic conductivity.
- Use directional freeze-casting to fabricate additive-free, dense electrodes with oriented low-tortuosity pore structure.
- Perform electrochemical testing of electrodes targeting area capacity of at least  $5\text{mAh/cm}^2$  under 1C continuous rate and  $10\text{mAh/cm}^2$  under 2C, 30 sec pulse.

# Milestones

Quarter	Milestones/Deliverables Description and Due Date
Q1 10/1/13- 12/31/13	Measure electronic and ionic conductivities and diffusivity in sintered dense $\text{Li}(\text{Ni},\text{Co},\text{Al})\text{O}_2$ (NCA) and Fe-doped high voltage spinel $\text{Li}_{1-x}\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ . Fabricate first freeze-cast samples of at least one cathode composition from (12/31/13). <b>Completed</b>
Q2 1/1/14-3/31/14	<b>Go/No-Go</b> Down select one cathode composition for follow-on work based on transport measurements and cycling tests of freeze cast and sintered electrodes (3/31/14) <b>Completed</b>
Q3 4/1/14-6/30/14	Demonstrate at least $5\text{mAh}/\text{cm}^2$ capacity per unit area at 1C continuous cycling rate for a freeze-cast cathode. (6/30/14)
Q4 7/1/14-9/30/14	Demonstrate at least $10\text{mAh}/\text{cm}^2$ capacity per unit area for a 2C 30 sec pulse for a freeze-cast cathode. (9/30/14)

# Approach

Independent measurement of the electronic and ionic conductivities by Electrochemical Impedance Spectroscopy (EIS) and Direct Current (DC) polarization techniques in a blocking cell configuration:

Electronic conductivity

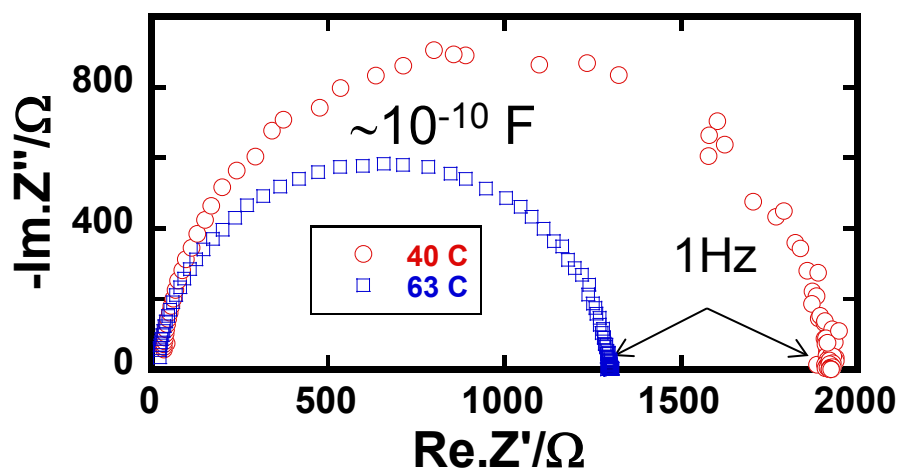


Ionically blocking cell

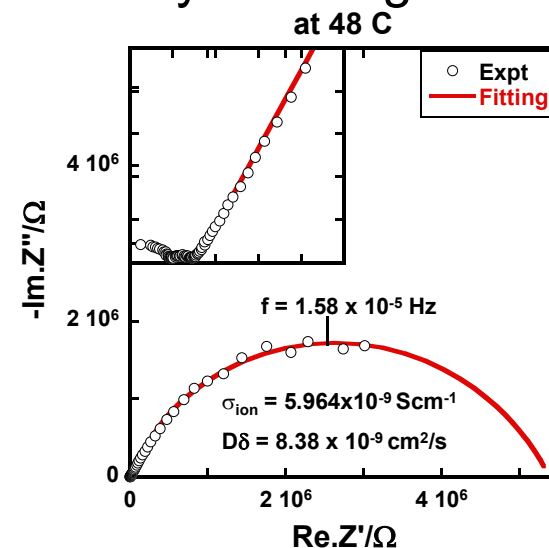
Ionic conductivity



Electronically blocking cell



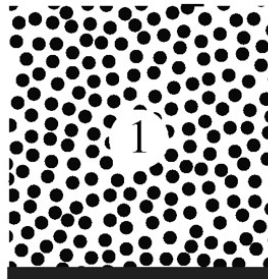
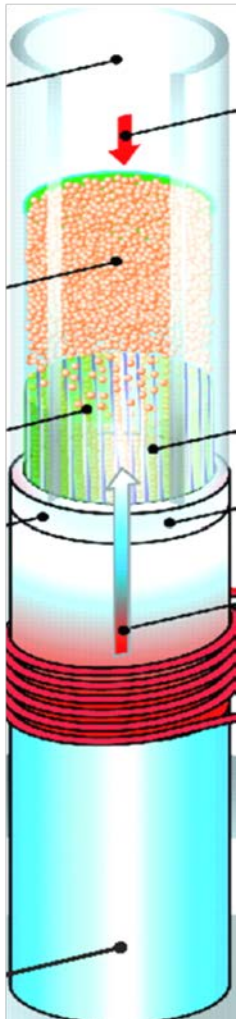
Impedance spectra of NCA  
( $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ )



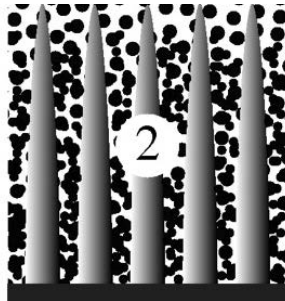
Impedance spectra of NCA

# Approach

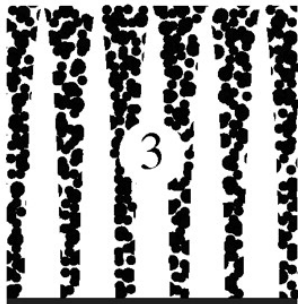
## Freeze-Casted Electrode Fabrication:



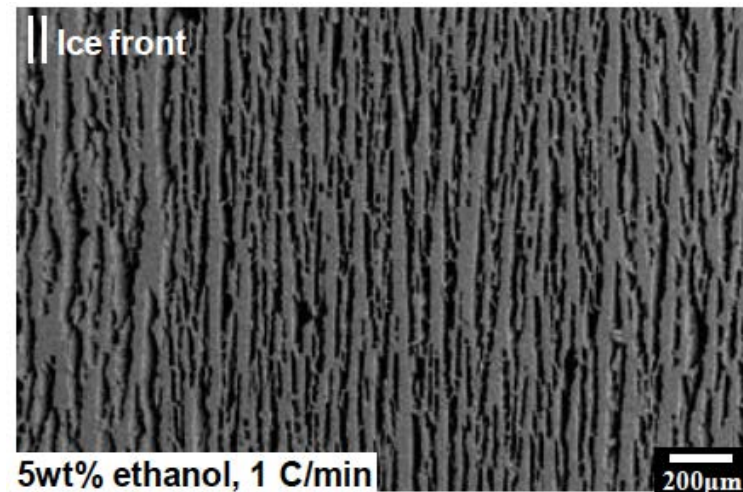
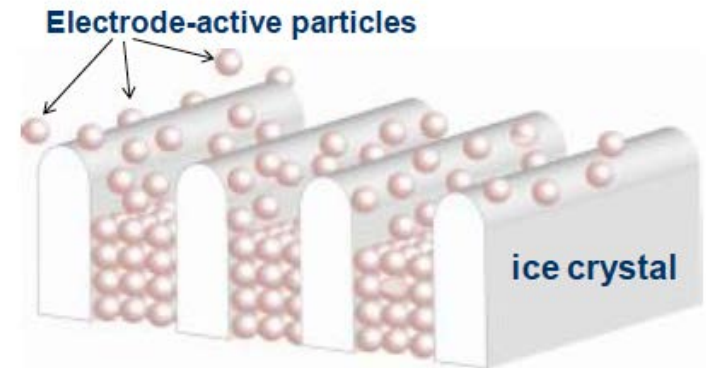
Slurry preparation



Solidification of the slurry



Sintering of the green body

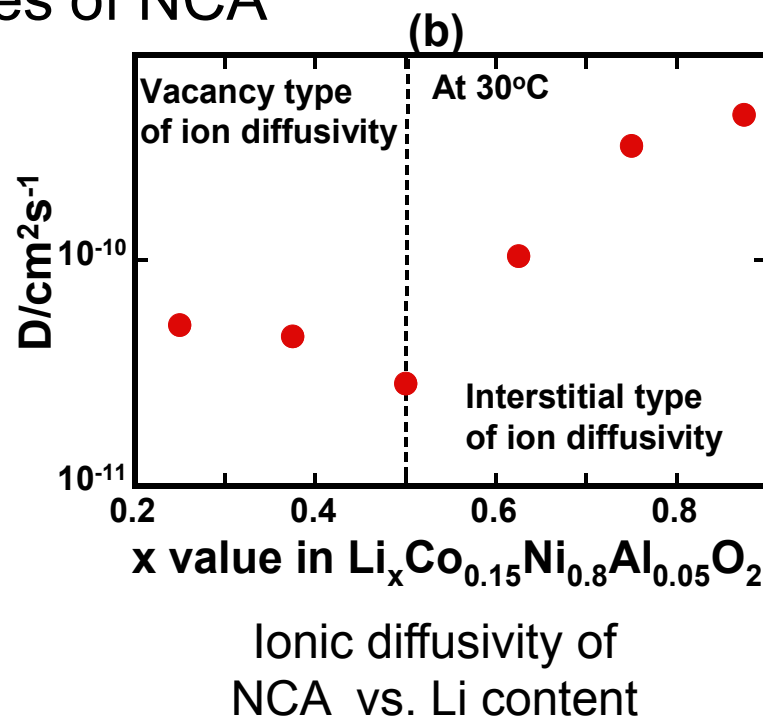
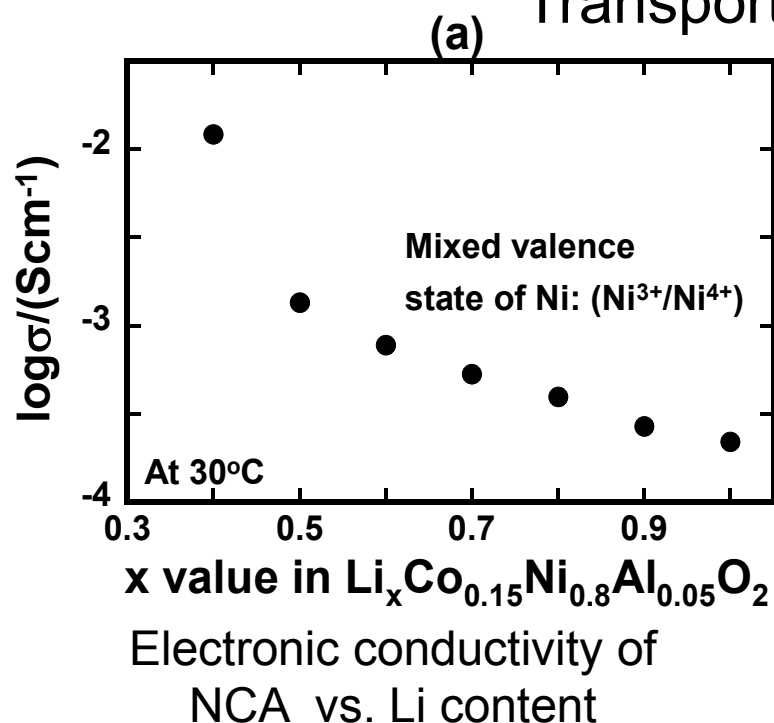


SEM micrograph of freeze casted LiCoO<sub>2</sub>

Schematic of freeze casting process

# Technical Accomplishments

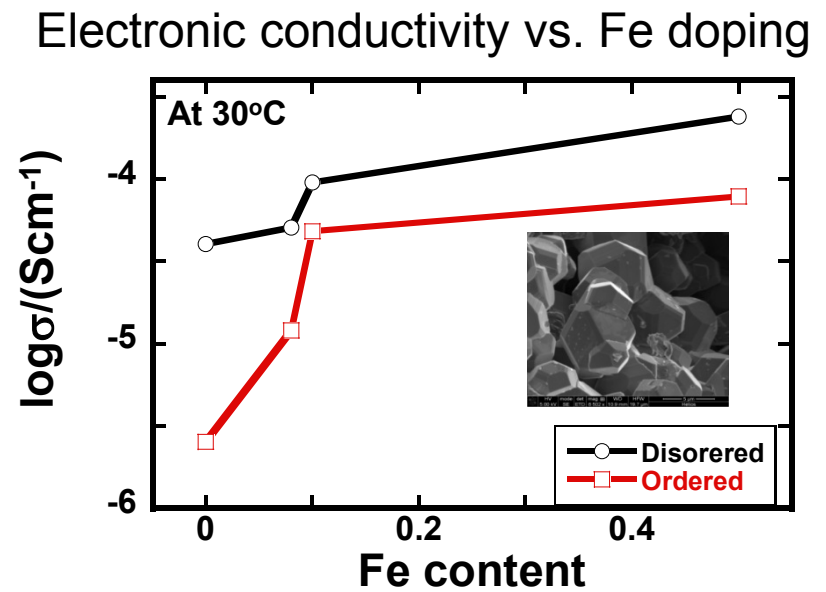
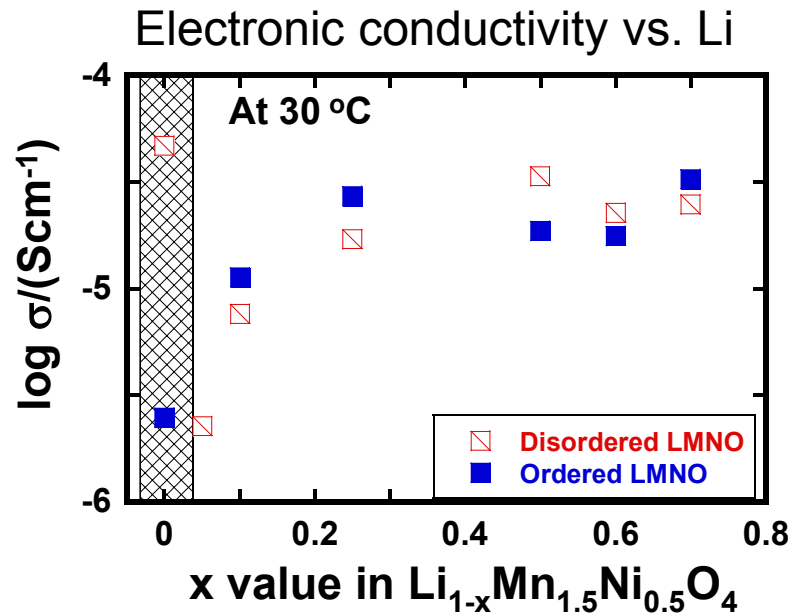
## Transport properties of NCA



- (a) NCA has  $\sim 10^{-4}$ – $10^{-3}$  S/cm electronic conductivity over the Li concentration range of interest. The electronic conductivity of NCA increases upon delithiation, but is always lower than that of LiCoO<sub>2</sub>.
- (b) It appears that lithium diffusion mechanism changes from interstitial type to vacancy type around 50% delithiation state. Obtained data can be functioned with the lamellae thickness up to 8  $\mu$ m for higher cycling rate.

# Technical Accomplishments

## The transport properties of LMNO and Fe-LMNO:

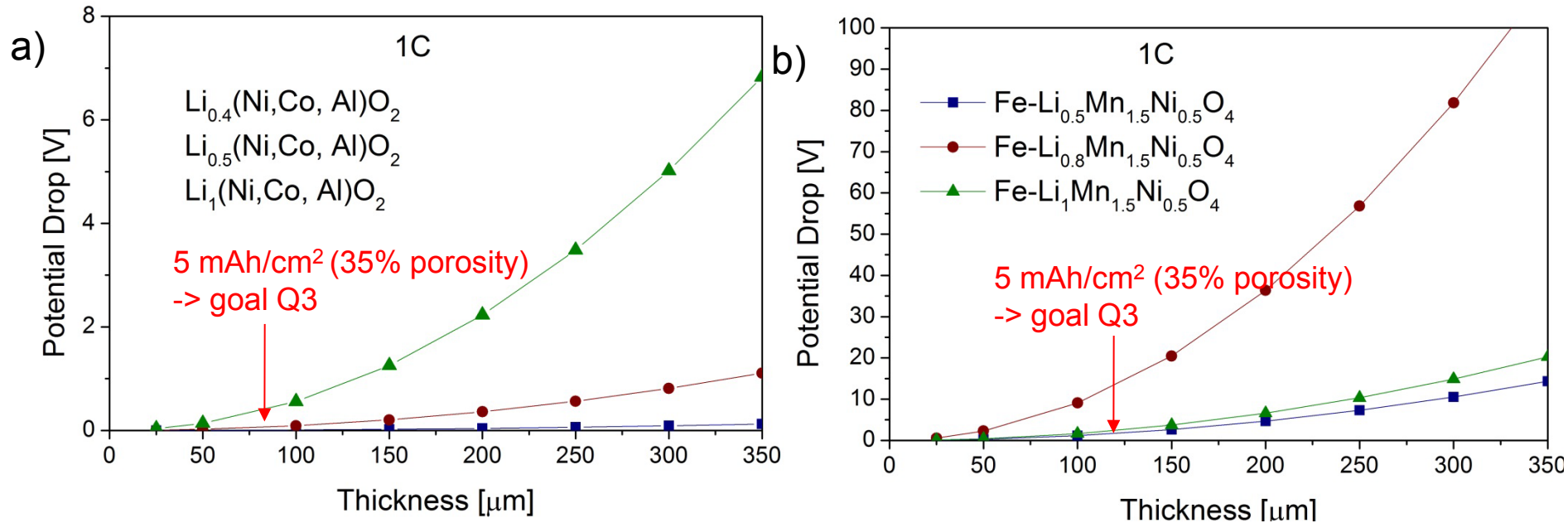


Samples (at 50°C)	Ionic conductivity (Scm <sup>-1</sup> )	Ionic diffusivity (cm <sup>2</sup> s <sup>-1</sup> )	
LiMn <sub>1.5</sub> Ni <sub>0.5</sub> O <sub>4</sub>	~2×10 <sup>-7</sup>	~10 <sup>-7</sup>	DC
LiMn <sub>1.5</sub> Ni <sub>0.5</sub> O <sub>4</sub>	~6×10 <sup>-8</sup>	~5×10 <sup>-8</sup>	AC
LiMn <sub>1.5</sub> Ni <sub>0.42</sub> Fe <sub>0.08</sub> O <sub>4</sub>	~8×10 <sup>-8</sup>	~6×10 <sup>-8</sup>	DC
LiMn <sub>1.5</sub> Ni <sub>0.42</sub> Fe <sub>0.08</sub> O <sub>4</sub>	~6×10 <sup>-8</sup>	~9×10 <sup>-8</sup>	AC

- Fe-LMNO selected for its resistance to electrochemical fracture
- Both LMNO and Fe-LMNO have a too low an electronic conductivity to use as a pure phase.
- Conductive additives would need to be incorporated for thick electrode applications.

# Technical Accomplishments

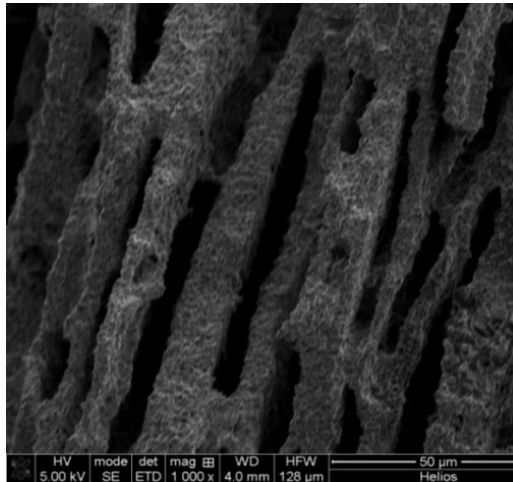
## Potential drop vs. electrode thickness for fully dense NCA and Fe-LMNO



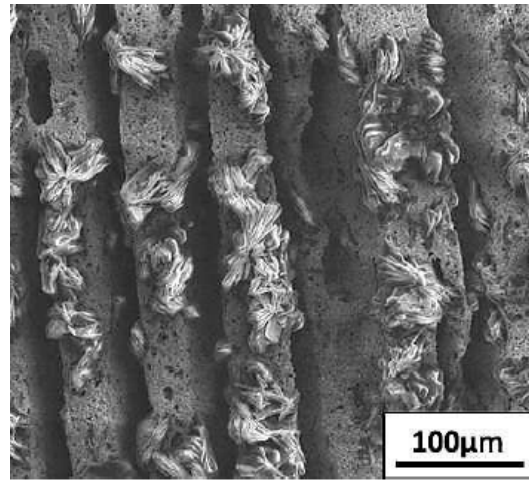
- Calculated for electronic conductivity at various Li contents. Note that cathodes in Li-ion cells are never fully lithiated after first cycle due to Li consumed in SEI formation
- Current density calculated on basis of measured capacities
- Potential drops are too large in Fe-doped LMNO to reach Q3 goal of 5 mAh/cm<sup>2</sup> at 1C rate – excluded from further consideration
- NCA to be evaluated further with electrochemical tests to establish true capacity vs. rate performance

# Technical Accomplishments

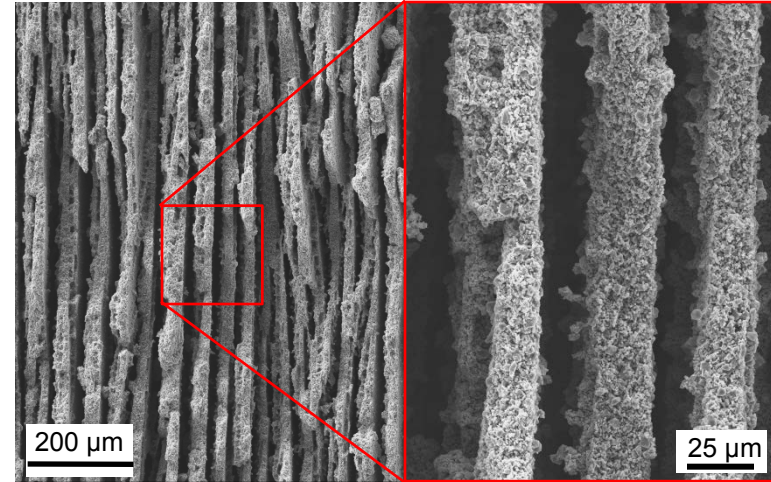
## Freeze-cast and sintered NCA and Fe-LMNO structures



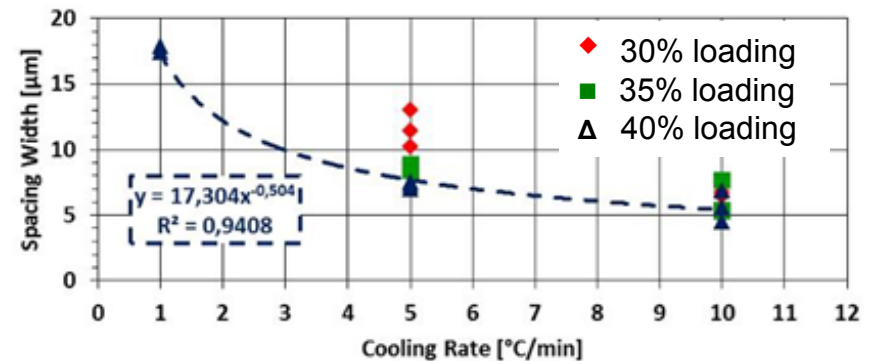
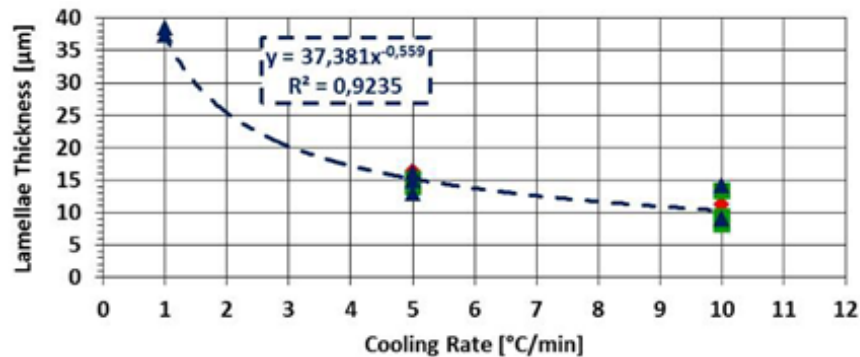
NCA



NCA



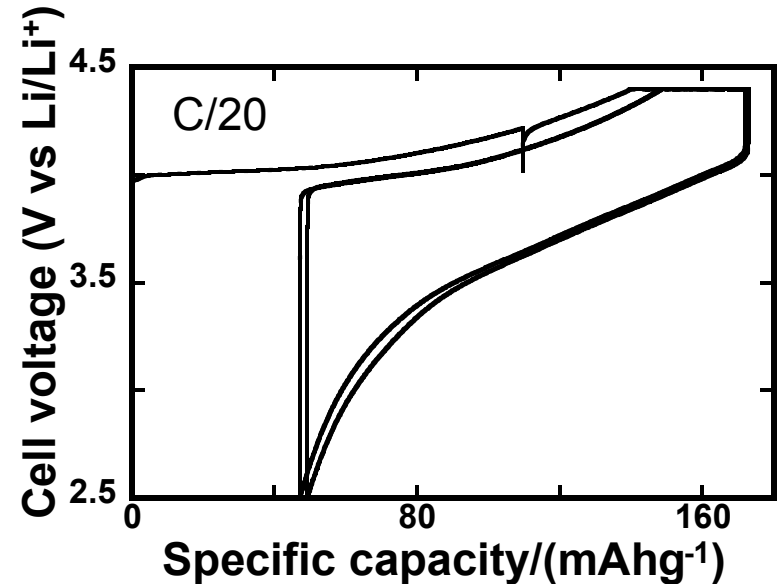
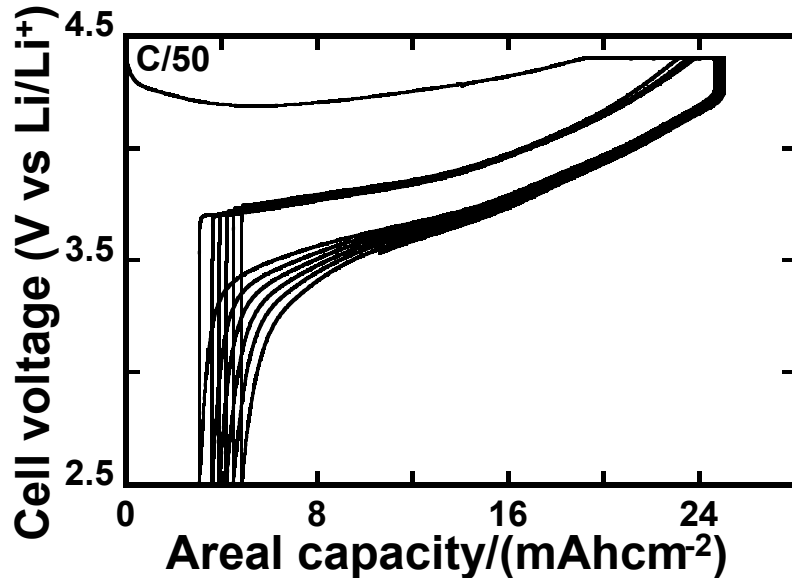
Fe-LMNO



- The freeze casting process was successfully adopted to both cathode materials
- The pores are penetrating at least over 600 μm
- The lamellae thickness can currently be varied from 40 μm to 10 μm
- The spacing width can currently be varied from 17 μm to 5 μm

# Technical Accomplishments

## Preliminary tests of freeze-cast and sintered NCA



- These initial electrodes have ~10 μm lamellae thickness, which is too large based on the solid phase ionic conductivity measurements
- At C/50, **24 mAh/cm<sup>2</sup>** areal capacity is available from a 520 μm thick electrode of 60-70% density (specific capacity is 160 mAh/g.)
- At C/20 the same electrode has 120mAh/g reversible capacity, and there is a clear increase in polarization
- Next experiments will focus on samples with smaller lamellae thickness

# Response to previous year Reviewer's Comments

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Not applicable – first year of project.

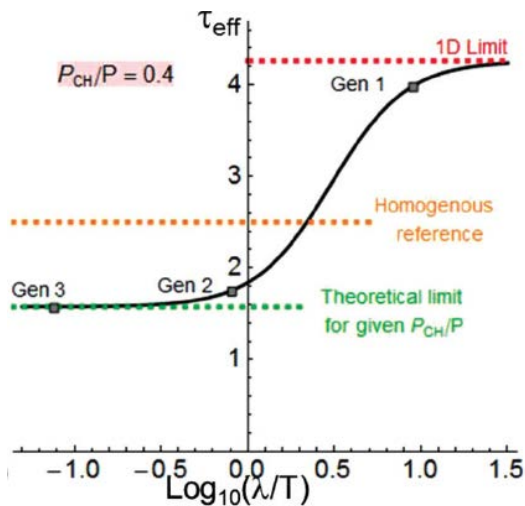
# Collaboration/Coordination with Other Institutions

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- Collaboration with A.P. Tomsia group at Lawrence Berkley National Laboratory (LBNL) for fabrication of directionally freeze-cast electrodes
- PI is member of BATT's Silicon Focus Group
- PI is member of BATT's High Voltage Cathode Focus Group and is Team Lead for Cathode Crystal Structure Transformations subgroup
- Dr. Jonathan Sander from ETH Zurich is self-supported member of BATT project working on alternative methods for pore alignment

# Remaining Challenges and Barriers

- Fabrication of thick dense electrodes with controlled dual-scale porosity: aligned pore channels having wall thickness below  $8\mu\text{m}$  and a higher degree of micro porosity in the walls.



*Previous calculations show that shorter channel spacing ( $\lambda$ ) for a given thickness  $T$  more effectively reduces the tortuosity and thus ion diffusion in the electrolyte.*

*Calculations also suggest that less than about 50% of the pore volume should be in the channels  $P_{\text{CH}}$  (Bae et al. Adv.Mater. 2013, 25, 1254–1258)*

- Developing a detailed model for transport across such electrodes, including continuous and pulse response.

# Proposed Future Work

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## Rest of FY 2014

- Tailor the microstructure in NCA in pursuit of the Milestones and Objectives of the project. Prepare and characterize comparative sintered porous samples without aligned pores. Revisit  $\text{LiCoO}_2$ .
- Demonstrate at least  $5\text{mAh/cm}^2$  capacity per unit area at 1C continuous cycling rate for a freeze-cast cathode.
- Demonstrate at least  $10\text{mAh/cm}^2$  capacity per unit area for a 2C 30 sec pulse for a freeze-cast cathode.

## FY 2015

- Initial development of directional freeze-casting in a planar geometry.
- Develop model to predict the impact of electronic conductivity on the ohmic potential drop in a porous electrode.
- Test best available cathodes in half-cells using USABC PHEV or EV protocols.
- Develop first additive-free anodes for use with microstructurally tailored cathodes.
- Incorporate Si anodes from the BATT Si Focus Group
- Construct and test full Li-ion cells

# Presentation Summary

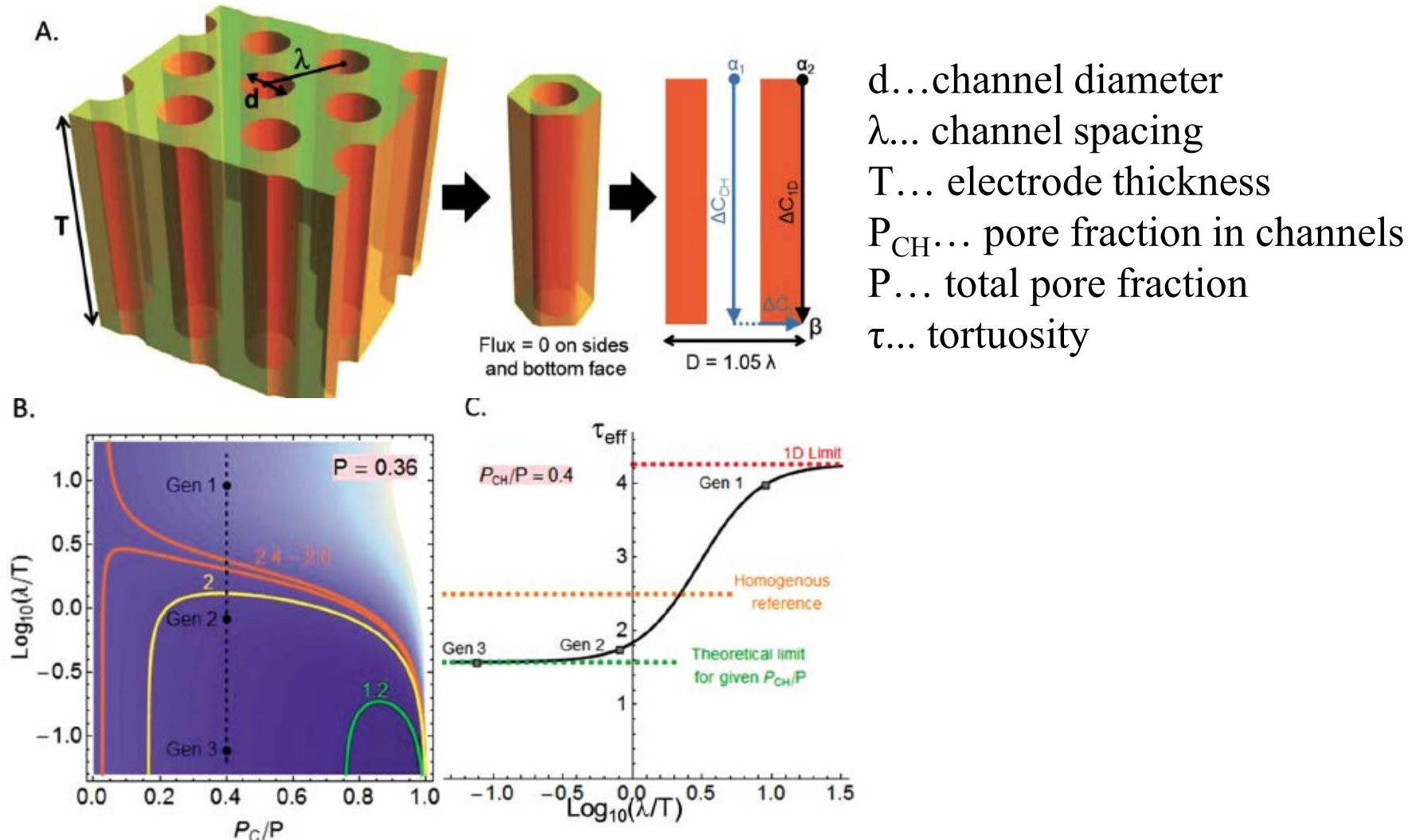
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- The electronic conductivity of the cathode is a critical parameter to obtain high area capacity ( $>10$  mAh/cm<sup>2</sup>) with dense additive-free electrodes. During the current fiscal year, the electronic and ionic conductivity of NCA, LMNO and Fe-LMNO (which is electrochemical-shock resistant) have been characterized.
- Of all the cathodes considered, NMC, LMNO and Fe-LMNO have been determined to have too low an electronic conductivity for use as additive-free electrodes. NCA and LCO (previously tested) have potential and will be further evaluated.
- Electrode structures with aligned pore channels have been successfully produced in NCA, LMNO and Fe-LMNO by directional-freeze casting. NMC and LiCoO<sub>2</sub> were previously demonstrated, and illustrate the generality of the approach
- The microstructure of the freeze-casted samples can be systematically varied (i.e. channel spacing and width) by controlling freeze-casting rate and sintering conditions

# Technical Back up slides

# Technical backup slide

## Influence of channel spacing and channel pore fraction on tortuosity



# Technical backup slide

## Estimation of Ohmic drop

$$\Delta V = RI = t^2 \frac{1}{\sigma} \rho(1-p) * Crate * Cap$$

$\Delta V$ ... voltage drop,  $R$ ... resistivity,  $I$ ... current [Ah],  $t$ ..., thickness,  $\rho$ ... density [g/cm<sup>3</sup>],  $A$ ... area: 1cm<sup>2</sup>,  $p$ ... porosity,  $Crate$  [1/h],  $Cap$ ... capacity [Ah/g],  $\sigma$ ... conductivity,

